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For and on behalf of RWS Group Ltd

The 21st day of April 2006

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Sieck

**Process for preparing alkyne-carboxylic acids by
oxidation of alkyne alcohols**

The present invention relates to a process for
5 oxidizing alkyne alcohols (alkynols) to
alkyne-carboxylic acids (alkynoic acids).

Alkynoic acids are important synthetic building blocks.
Of particular importance are propiolic acid and
10 acetylenedicarboxylic acid which are used to build
rings in cycloadditions, in particular Diels-Alder
reactions and 1,3-dipolar cycloadditions, and in
nucleophilic addition reactions (overview in Ullmann's
Encyclopedia, 6th Edition, 2001 electronic release;
15 "Carboxylic acids, aliphatic 5.2").

The oxidation of alkynols to alkynoic acids has been
described in the prior art (overviews in Ullmann's
Encyclopedia, 6th Edition, 2001 electronic release;
20 "Carboxylic acids, aliphatic 5.2"; Houben-Weyl volume
V/2a, 4th edition 1977, "Alkynes").

For example, propiolic acid is obtained by anodic
oxidation of propargyl alcohol (Wolf, Chem. Ber. 1954,
25 87, 668). Acetylenedicarboxylic acid is likewise
obtained by anodic oxidation of 2-butyne-1,4-diol.
However, the electrochemical process has the
disadvantage of the use of lead dioxide anodes which
leads to the contamination of the electrolytes with
30 lead ions and can generally only be used in production
at high capital cost. In addition, the decarboxylation
of the product proceeding as a side reaction leads to
technically undesired formation of large amounts of CO₂
and acetylene which have to be disposed of. Also, the

yields in the case of propiolic acid are relatively low (less than 50%).

5 The analogous anodic oxidation on nickel oxide anodes (Kaulen and Schäfer, Tetrahedron 1982, 38, 3299) requires low current densities and very large electrode surface areas, which leads to a further increase in the capital costs. In addition, the activated nickel surface is passivated during the electrolysis and
10 frequently has to be regenerated which leads to an increase in the process costs.

Propiolic acid can also be obtained by oxidation of propargyl alcohol with Cr(VI) oxide in sulfuric acid.
15 Good yields can be achieved, but large amounts of toxic and environmentally hazardous heavy metal salts have to be disposed of. The analogous reaction of 2-butyne-1,4-diol leads to only a 23% yield of acetylenedicarboxylic acid (Heilbron, Jones and Sondheimer,
20 J. Chem. Soc. 1949, 606).

A known nonoxidative preparation process of propiolic acid and acetylenedicarboxylic acid is the reaction of metal acetylides with CO_2 . However, this requires the
25 use of expensive metal bases and, owing to the use of acetylene, is technically not without risk. The yields of this process in the case of propiolic acid are likewise only 50%.

30 In a further process for preparing acetylenedicarboxylic acid, fumaric acid is initially converted with bromine to meso-dibromosuccinic acid, which is then isolated and dehalogenated in a further stage. This two-stage process is time-consuming and

laborious (T.W. Abbott et al., Org. Synth. Coll. Vol. II, 1943, 10).

5 The prior art discloses general oxidation processes of alcohols to carboxylic acids with the aid of nitroxyl compounds as catalysts, in particular with the aid of nitroxyls such as TEMPO (2,2,6,6-tetramethylpiperidine 1-oxyl) and its derivatives (overview in A.E.J. de Nooy, A.C. Besemer and H.V. Bekkum, Synthesis 1996,
10 1153).

TEMPO-catalyzed oxidations of alcohols to carboxylic acids are carried out in biphasic systems, for example methylene chloride/water and also in the presence of
15 phase transfer catalysts (G. Grigoropoulou et al., Chem. Commun. 2001, 547-548, P.L. Anelli, C. Biffi, F. Montanari and S. Quici, J. Org. Chem. 1987, 52, 2559). The stoichiometric oxidant used is predominantly bleaching liquor (hypochlorite solution).

20 In the customary performance of these syntheses in biphasic systems, the oxidant dissolved in the aqueous phase, which is adjusted to a pH range of 8.5-9, is added in a batch process to an initially charged
25 organic phase which comprises the alcohol to be oxidized, the phase transfer catalyst and the nitroxyl compound.

30 The prior art discloses that such oxidation processes using bleaching liquor and nitroxyl compounds are generally to be considered as unsuitable for the oxidation of unsaturated alcohols (on this subject, compare in particular P.L. Anelli, C. Biffi, F. Montanari and S. Quici, J. Org. Chem. 1987, 52, 2559;

P.L. Anelli, F. Montanari and S. Quici, *Org. Synth.*, 1990, 69, 212).

For instance, the reaction of an alkyne alcohol without terminal alkyne group (3-phenylpropynol) with bleaching liquor and TEMPO by the process disclosed in the prior art affords only unacceptable low yields of from 5 to a maximum of 20 mol% of the alkynoic acid (M. Zhao et al., *J. Org. Chem.* 1999, 64, 2564; WO 99/52849).

10 The oxidation of alkynols with terminal alkyne group with bleaching liquor and TEMPO at pH > 7 has hitherto not been described.

A possible cause is the sensitivity disclosed by the literature of terminal alkyne groups toward bleaching liquor. The CH groups of terminal alkynes are easily converted, for example, to chloroalkynes by bleaching liquor, which are particularly labile in alkaline media and tend to decompose (Straus et al., *Ber. Dtsch. Chem. Ges.* 1930, 1868). This is especially true in the case of alkaline reaction conditions, since the acidic terminal acetylene unit is particularly readily halogenated. The resulting 3-halopropiolates are additionally compounds which decompose easily and have a tendency toward explosion.

It is therefore an object of the present invention to provide a process for preparing alkynoic acids by the oxidation of alkyne alcohols which avoids the disadvantages known from the prior art.

Surprisingly, it has now been found that the disadvantages of the processes disclosed by the prior art can be avoided by not initially charging all of the

alkyne alcohol to be oxidized in the presence of nitroxyl compounds at $\text{pH} > 7$, as in the processes disclosed by the prior art, but rather by adding it to the reaction mixture continually, like the oxidant.

5

The invention therefore provides a process for preparing alkynecarboxylic acids, characterized by the oxidation of an alkyne alcohol with a hypohalite in the presence of a nitroxyl compound at a pH of > 7 , with
10 continual addition of the alkyne alcohol and of the hypohalite to the reaction mixture.

The continual addition of the alkyne alcohol and of the hypohalite to the reaction mixture in accordance with
15 the process according to the invention may be continuous or discontinuous.

In the case of continuous addition, a greater or lesser amount, depending on various reaction parameters to be
20 monitored, of alkyne alcohol and hypohalite is metered in constantly.

In the case of discontinuous addition, alkyne alcohol and hypohalite, depending on various reaction
25 parameters to be monitored, are metered in intermittently.

The continual addition of the alkyne alcohol and of the hypohalite to the reaction mixture, both in the case of
30 the continuous and the discontinuous method, may be parallel or alternating.

In the case of alternating addition, alkyne alcohol and hypohalite are not metered in simultaneously and/or are

not metered in in the same molar amounts within a time interval.

In the case of parallel addition, alkyne alcohol and
5 hypohalites are always metered in simultaneously
(parallel addition).

The reaction parameters to be monitored in the case of
the continual addition of the alkyne alcohol and of the
10 hypohalites to the reaction mixture relate in
particular to the pH of the reaction mixture and also
to its temperature.

In a particularly preferred embodiment of the
15 invention, alkyne alcohol and hypohalite are added
continually and in parallel.

In a preferred embodiment of the process according to
the invention, an initial charge can be used which may
20 comprise water, one or more inert organic solvents,
acids, bases or buffer mixtures, portions or the entire
amounts of the nitroxyl compounds and phase transfer
catalysts used, and also portions of the alkyne alcohol
used or portions of the oxidant used.

25

The conversion is then effected by further continual
addition of the alkyne alcohol and of the hypohalite to
the initial charge.

30 The use of an initial charge is recommended in
particular for the beginning of a continuous reaction.

It has also been found that, surprisingly, alkyne alcohols can also be oxidized to alkynecarboxylic acids without the use of phase transfer catalysts.

5 Surprisingly, the oxidation is possible even in an aqueous monophasic system.

It has also been found that, surprisingly, alkyne alcohols having terminal alkyne groups can also be
10 oxidized in excellent yields at $\text{pH} > 7$ by the process according to the invention.

In general, the alkyne alcohols (alkynols) to be oxidized are compounds which contain at least one
15 monovalent group of the formula $-\text{CH}_2-\text{OH}$ and at least one divalent group of the formula $-\text{C}\equiv\text{C}-$.

The alkyne alcohols to be oxidized are preferably linear or branched primary alcohols having 3-30 carbon
20 atoms, cyclic alcohols having 8-30 carbon atoms or alcohols which are substituted by an aromatic radical and have 6-30 carbon atoms, each of which contains a group of the formula $-\text{C}\equiv\text{C}-$,

25 where one hydrogen or more than one hydrogen may be independently replaced by F, Cl, Br, I, NO_2 , ONO , CN , NC or SCN ,

or where one CH_2 group or more than one CH_2 group may be
30 independently replaced by O, NH , $\text{C}=\text{O}$, CO_2 , S, $\text{S}=\text{O}$, SO_2 , $\text{P}=\text{O}$ or PO_2 ,

or one CH group or more than one CH group may be independently replaced by N, B or P, or quaternary carbon atoms may be replaced by Si, Sn or Pb.

5 Particular preference is given to the alkyne alcohols $R^1-C\equiv C-CH_2OH$, $R^1-C\equiv C-CH_2-CH_2OH$ or $R^1C\equiv C-CH_2-CH_2-CH_2OH$, $R^1-O-CR^2R^3-C\equiv C-CH_2OH$, $R^1-O-CR^2R^3-C\equiv C-CH_2-CH_2OH$ or $R^1-O-CR^2R^3-C\equiv C-CH_2-CH_2-CH_2OH$

10 where R^1 is H, methyl, ethyl or a linear or branched C_3-C_{12} radical, in particular an n-propyl, isopropyl, 1- or 2-n-butyl, 2-methylpropyl, 1-, 2- or 3-n-pentyl, 2- or 3-methyl-1-butyl, 1,2-dimethylpropyl, tert-butyl, neopentyl or tert-pentyl radical,

15 or a saturated or unsaturated cyclic C_3-C_{12} radical, in particular a cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, methylcyclopentyl, methylcyclopentenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl, methylcyclohexenyl, 20 cycloheptyl, cyclooctyl, cyclododecyl or decalanyl radical

or a C_6-C_{12} -aryl or aralkyl radical, in particular a phenyl, benzyl, phenethyl, naphthyl, biphenyl, 25 anthryl, phenanthryl, azulenyl, anthraquinonyl, 2-, 3- or 4-methylphenyl, 2,3-, 2,4- or 2,5-dimethylphenyl or mesityl radical,

or a C_6-C_{12} -heteroaryl or heteroaralkyl radical, in 30 particular a furyl, pyrrolyl, thienyl, benzofuranyl, isobenzofuranyl, benzothiyl, isobenzothienyl, indolyl, isoindolyl, indoliziny, pyrazolyl, imidazolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, indazolyl, carbazolyl, benzotriazolyl, purinyl,

pyridyl, pyridazinyl, pyrimidyl, pyrazinyl, quinolinyl, isoquinolinyl, quinoxalinyl, quinazolinyl, cinnolinyl, phenanthridinyl, acridinyl, 1,10-phenanthrolinyl, phenazinyl, phenothiazinyl or phenoxazinyl radical,

5

or is $R^4R^5R^6Si$ where R^4 , R^5 and R^6 are each independently C_1 - C_{12} -alkyl, in particular methyl, ethyl, n-propyl, isopropyl or n-butyl,

10 or C_1 - C_{12} -oxyalkyl, in particular methoxy, ethoxy, n-propoxy, isopropoxy or butoxy,

C_6 - C_{12} -aryl or C_7 - C_{12} -aralkyl, in particular phenyl or benzyl,

15

and R^2 and R^3 are each independently H, C_1 - C_{12} -alkyl, in particular methyl, ethyl, n-propyl or n-butyl,

C_6 - C_{12} -aryl or C_7 - C_{12} -aralkyl, in particular phenyl, 2-,
20 3- or 4-methylphenyl or benzyl,

and to alkynols $R^7-CO-C\equiv C-CH_2OH$, $R^7-CO-C\equiv C-CH_2-CH_2OH$ or $R^7-CO-C\equiv C-CH_2-CH_2-CH_2OH$ where R^7 is methyl, ethyl or a linear or branched C_3 - C_{12} radical, in particular an
25 n-propyl, isopropyl, 1- or 2-n-butyl, 2-methylpropyl, 1-, 2- or 3-n-pentyl, 2- or 3-methyl-1-butyl, 1,2-dimethylpropyl, tert-butyl, neopentyl or tert-pentyl radical,

30 or a saturated or unsaturated cyclic C_3 - C_{12} radical, in particular a cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, methylcyclopentyl, methylcyclopentenyl, cyclohexyl, cyclohexenyl, methylcyclohexyl,

methylcyclohexenyl, cycloheptyl, cyclooctyl, cyclododecyl or decalinyl radical

or a C₆-C₁₂-aryl or aralkyl radical, in particular a
5 phenyl, benzyl, phenethyl, naphthyl, biphenyl, anthryl, phenanthryl, azulenyl, anthraquinonyl, 2-, 3- or 4-methylphenyl, 2,3-, 2,4- or 2,5-dimethylphenyl or mesitylyl radical,

10 or a C₆-C₁₂-heteroaryl or heteroaralkyl radical, in particular a furyl, pyrrolyl, thienyl, benzofuranyl, isobenzofuranyl, benzothiyl, isobenzothienyl, indolyl, isoindolyl, indoliziny, pyrazolyl, imidazolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl,
15 indazolyl, carbazolyl, benzotriazolyl, purinyl, pyridyl, pyridazinyl, pyrimidyl, pyrazinyl, quinolinyl, isoquinolinyl, quinoxalinyl, quinazolinyl, cinnolinyl, phenanthridinyl, acridinyl, 1,10-phenanthrolinyl, phenazinyl, phenothiazinyl or phenoxazinyl radical,

20

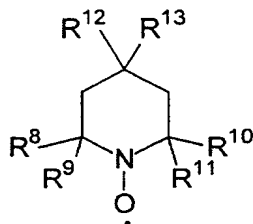
and also to Cl-CH₂-C≡C-CH₂OH and HO-CH₂-C≡C-CH₂OH.

Very particular preference is given to 2-propyn-1-ol, but-3-yn-1-ol, but-2-yn-1-ol, pent-4-yn-1,2-diol,
25 2-butyn-1,4-diol, 4-chloro-2-butyn-1-ol, 4-acetoxy-2-butyn-1-ol, 4-t-butyldimethylsiloxy-2-butyn-1-ol, 3-phenyl-2-propyn-1-ol, 3-trimethylsilyl-2-propyn-1-ol, 3-t-butyldimethylsilyl-2-propyn-1-ol.

30 In particular, 2-propyn-1-ol, 4-chloro-2-butyn-1-ol or 2-butyn-1,4-diol are suitable, most preferably 2-propyn-1-ol or 2-butyn-1,4-diol.

The nitroxyl compound used as an oxidation catalyst is generally a di-tert-alkylnitroxyl compound.

It is preferably a nitroxyl compound of the general
5 formula I



I

where the radicals R⁸, R⁹, R¹⁰ and R¹¹ are each indepen-
10 dently C₁-C₁₂-alkyl or C₂-C₁₂-alkenyl or C₆-C₁₂-aryl or
aralkyl,

and the radicals R¹² and R¹³ are each independently
hydrogen, OH, CN, halogen,

15

linear or branched, saturated or unsaturated C₁-C₂₀-
alkyl, C₆-C₂₀-aryl, C₆-C₂₀-hetaryl or C₆-C₂₀-aralkyl, OR¹⁴,
O-COR¹⁴, O-COOR¹⁴, OCONHR¹⁴, COOH, COR¹⁴, COOR¹⁴, CONHR¹⁴

20 where R¹⁴ is a linear or branched, saturated or
unsaturated C₁-C₂₀-alkyl radical, or a C₆-C₂₀-aryl, C₃-C₂₀-
hetaryl or C₆-C₂₀-aralkyl radical,

- (O-CH₂-CH₂)_n-OR¹⁵, - (O-C₃H₆)_n-OR¹⁵, - (O-(CH₂)₄)_n-OR¹⁵,
25 -O-CH₂-CHOH-CH₂-(O-CH₂-CH₂-)_n-OR¹⁵

where R¹⁵ is hydrogen, C₁-C₂₀-alkyl, C₆-C₂₀-aralkyl, where
n = 1 to 100, or CH₂-CHOH-CH₃ or CH₂-CHOH-CH₂-CH₃,

$\text{NR}^{16}\text{R}^{17}$, NHCOR^{16} , NHCOOR^{16} , NHCONHR^{16} ,

where R^{16} and R^{17} are each independently a linear or
branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ -alkyl radical,
5 a $\text{C}_6\text{-C}_{12}$ -cycloalkyl radical, or a $\text{C}_6\text{-C}_{20}$ -aryl, $\text{C}_3\text{-C}_{20}$ -
hetaryl or $\text{C}_6\text{-C}_{20}$ -aralkyl radical,

where the radicals R^{12} and R^{13} may also be linked to a
ring,

10

and where the radicals R^{12} and R^{13} in turn may also be
substituted by COOH , OH , SO_3H , CN , halogen, primary,
secondary or tertiary amino or quaternary ammonium,

15 or the radicals R^{12} and R^{13} together may also be $=\text{O}$,
 $=\text{NR}^{18}$, $=\text{N-OR}^{18}$, $=\text{N-N=CR}^{18}\text{R}^{19}$ where R^{18} and R^{19} are each
independently hydrogen, $\text{C}_1\text{-C}_{20}$ -alkyl or $\text{C}_6\text{-C}_{20}$ -aralkyl.

Preference is further given to the nitroxyl compound
20 being two molecules of the formula I which are linked
via a bridge $=\text{N-N=}$ in the 4-position.

Preference is further given to the nitroxyl compound
being two or more molecules of the formula I which are
25 bonded to each other via one of the two radicals R^{12} and
 R^{13} . The linking radical is particularly preferably
 O-alkyl-O , $\text{O-CH}_2\text{-aryl-CH}_2\text{-O}$, or a bridge of the general
formula $(\text{O}-(\text{CH}_2)_n\text{-O})_m$ where $n = 2$ to 4 and $m = 2$ to 50 ,
in particular $m = 2$ to 20 .

30

In a further embodiment, the nitroxyl compound is a
polymeric structure comprising compounds of the
formula I which are linked via the radicals R^{11} or R^{12} or
 R^{11} and R^{12} .

Those skilled in the art are familiar with a variety of such compounds from the prior art (EP 1103537, Cirriminna et al., Chem. Commun. 2000, 1441; Bolm et al., Chem. Commun. 1999, 1795; Bobbitt et al., Chem. Commun. 1996, 2745, Miyazawa and Endo, J. Molec. Catal. 49, 1988, L31; M.J. Verhoef et al. in "Studies in Surface Science and Catalysis", Vol. 125, p. 465 ff; D. Brunel et al. in "Studies in Surface Science and Catalysis", Vol. 125, p. 237 ff; Miyazawa and Endo, J. Polymer Sci., Polym. Chem. Ed. 23, 1985, 1527 and 2487; T. Osa, Chem. Lett. 1988, 1423).

In particular, PIPO (polyamine-immobilized piperidinyl oxyl), SiO₂-supported TEMPO, polystyrene- and polyacrylic acid-supported TEMPO are particularly suitable.

Particularly preferred nitroxyl compounds are compounds of the general formula I, where R⁸, R⁹, R¹⁰ and R¹¹ are each CH₃

and R¹² and R¹³ are each independently hydrogen, OH, OR¹⁴, O-COR¹⁴, O-COOR¹⁴, OCONHR¹⁴,

where R¹⁴ is a linear or branched, saturated or unsaturated C₁-C₂₀-alkyl radical, or a C₆-C₂₀-aryl or C₆-C₂₀-aralkyl radical,

$-(O-CH_2-CH_2)_n-OR^{15}$, $-(O-C_3H_6)_n-OR^{15}$, $-(O-(CH_2)_4)_n-OR^{15}$,
 $-O-CH_2-CHOH-CH_2-(O-CH_2-CH_2-)_n-OR^{15}$

where R¹⁵ is hydrogen, C₁-C₁₀-alkyl or C₆-C₁₀-aralkyl, where n = 1 to 100, or CH₂-CHOH-CH₃ or CH₂-CHOH-CH₂-CH₃,

$\text{NR}^{16}\text{R}^{17}$, NHCOR^{17} , NHCOOR^{17} , NHCONHR^{17} ,

where R^{16} and R^{17} are each independently hydrogen, a linear or branched, saturated or unsaturated $\text{C}_1\text{-C}_{20}$ -alkyl radical, a $\text{C}_6\text{-C}_{12}$ -cycloalkyl radical or a $\text{C}_6\text{-C}_{20}$ -aryl or $\text{C}_6\text{-C}_{20}$ -aralkyl radical.

Further particularly preferred nitroxyl compounds are compounds of the general formula I where R^8 , R^9 , R^{10} and R^{11} are each CH_3 ,

where R^{12} and R^{13} together form ketal groups of the formulae $\text{O-CHR}^{20}\text{CHR}^{21}\text{-O}$ or $\text{O-CH}_2\text{CR}^{22}\text{R}^{23}\text{-CH}_2\text{-O}$ where R^{20} , R^{21} , R^{22} and R^{23} are each independently hydrogen or $\text{C}_1\text{-C}_3$ -alkyl,

or where the radicals R^{12} and R^{13} together are $=\text{O}$.

A preferred nitroxyl compound is in particular a compound of the general formula I where R^8 , R^9 , R^{10} and R^{11} are each CH_3 ,

where R^{12} is hydrogen and R^{13} is hydrogen, OH , OR^{14} , O-COR^{14} ,

where R^{14} is a linear or branched saturated $\text{C}_1\text{-C}_{12}$ -alkyl radical, or is an aryl or benzyl radical,

$-(\text{O-CH}_2\text{-CH}_2)_n\text{-OR}^{15}$, $-(\text{O-C}_3\text{H}_6)_n\text{-OR}^{15}$, $-(\text{O-(CH}_2)_4)_n\text{-OR}^{15}$,
 $-\text{O-CH}_2\text{-CHOH-CH}_2\text{-(O-CH}_2\text{-CH}_2\text{)}_n\text{-OR}^{15}$ where $n = 1$ to 50

and R^{15} is hydrogen or $\text{CH}_2\text{-CHOH-CH}_3$ or $\text{CH}_2\text{-CHOH-CH}_2\text{-CH}_3$

NR¹⁶R¹⁷, NHCOR¹⁷ where R¹⁶ and R¹⁷ are each independently a linear or branched, saturated C₁-C₁₂-alkyl radical or an aryl or benzyl radical.

5 Examples of nitroxyl compounds which can be used with particular preference are TEMPO, 4-hydroxy-TEMPO, 4-oxo-TEMPO, 4-amino-TEMPO, 4-acetamido-TEMPO, 4-benzoyloxy-TEMPO, 4-acetoxy-TEMPO and PIPO.

10 4-Hydroxy-TEMPO is most preferred.

The nitroxyl compound is generally used in amounts of from 0.01 to 50 mol%, preferably in amounts of from 0.1 to 20 mol%, more preferably in amounts of from 1 to
15 10 mol%, based on the amount of alkyne alcohol to be oxidized.

The nitroxyl compound may be dissolved in the reaction component comprising the alkyne alcohol or in the
20 aqueous phase or used in supported form as an independent phase. The nitroxyl compound can be initially charged in its entirety or be added continuously to the reaction mixture, optionally also in the form of an additional liquid feed.

25

The oxidant used is preferably a compound selected from the group of the hypohalites, in particular hypochlorite, hypobromite and hypoiodite or their mixtures. A particularly preferred oxidant is
30 hypochlorite. Preferred counterions are hydrogen, sodium, potassium, calcium or tetraalkylammonium and particular preference is given to sodium and calcium.

Those skilled in the art are familiar with suitable hypohalites and hypohalite preparations from the prior art (Ullmann Encyclopedia, 6th Edition, 2002 electronic release; "Chlorine oxides and Chlorine oxygen acids
5 2. - 4.").

In a particularly preferred embodiment, technical hypohalite solutions and suspensions, in particular technical hypochlorite solutions, are used.

10 The oxidant used may also be generated in situ, in particular electrochemically, by hydrolysis, in particular by hydrolysis of N-chlorine compounds, or by redox reactions such as, in the case of hypochlorite or hypobromite solutions, by the disproportionation of
15 chlorine or bromine in aqueous alkaline solution, or by the redox reaction between hypochlorite and bromide which leads to the formation of hypobromite.

The oxidants used, in particular hypochlorite and hypobromite are preferably used as aqueous solutions in
20 concentrations of from 0.1 M up to their respective saturation concentration.

The pH of aqueous solutions or suspensions of the
25 oxidant is generally from 7 to 14. However, it is not necessary to adjust the pH of the oxidant to a particular value, so that adjustment of the pH of the oxidant beforehand can advantageously be dispensed with.

30

The pH of the aqueous phase of the reaction mixture in the process according to the invention is thus a pH of greater than 7, preferably between pH 7 and 14, more

preferably between pH 7 and 11, in particular between pH 8 and 10.

5 Preference is given to using from 2 to 5 mol equivalents of the hypohalite based on the number of functional groups to be oxidized, in particular from 2 to 3 mol equivalents of the hypohalite based on the number of functional groups to be oxidized.

10 The desired pH of the reaction mixture is generally attained by adding a base, preferably sodium hydroxide, potassium hydroxide, calcium hydroxide, calcium carbonate, sodium carbonate, more preferably sodium hydroxide and calcium carbonate.

15 The desired pH of the reaction mixture can also be attained by adding a buffer, preferably by adding a carbonate or phosphate buffer. From the group of the carbonate buffers, particularly suitable are sodium
20 carbonate/sodium hydrogencarbonate or calcium carbonate/calcium hydrogencarbonate, in particular calcium carbonate/calcium hydrogencarbonate. From the group of the phosphate buffers, particularly suitable are sodium salts or potassium salts of phosphoric acid.
25 Further possible additives are salts, for example alkali metal, alkaline earth metal or ammonium halides, carbonates or sulfates.

The reaction temperature is generally from -10 to
30 +80°C, preferably from -5 to +40°C, more preferably from -5 to +20°C.

The process according to the invention is preferably carried out at atmospheric pressure.

Generally, the components involved in the reaction in the process according to the invention can be reacted in one phase or divided between a plurality of phases.

5 In one possible embodiment, the process according to the invention is carried out in a liquid phase which comprises water and one or more water-miscible solvents (cosolvents).

10 In one embodiment of the monophasic reaction, the alkyne alcohol to be oxidized is added in pure form or eluted with water or with one or more inert, water-miscible solvents, as reaction component 1, and the oxidant as reaction component 2.

15

The inert, water-miscible solvents are preferably selected from the group of the ethers, in particular THF and 1,4-dioxane, the nitriles, in particular acetonitrile or alcohols, for example tert-butanol,
20 isopropanol or DMF, DMSO.

The alkyne alcohol to be oxidized can be used in concentrations of between 0.1 and 100% by weight, preferably between 20 and 100% by weight, based on
25 reaction component 1.

In a further possible embodiment of the process according to the invention, the reactions are carried out in multiphasic systems.

30

In this case, preference is given to using at least one aqueous phase and one organic phase.

In a particularly preferred embodiment, the alkyne alcohol is used as reaction component 1, optionally in pure form or dissolved in one or more solvents. Preference is given to using water-immiscible organic solvents. The resulting phase separation may be caused by a water-immiscible alkyne alcohol as a reactant.

The aqueous phase as reaction component 2 comprises the oxidant.

10

Preferred organic solvents for carrying out the process according to the invention in a multiphasic system are one or more solvents selected from the group of ethers, in particular THF, methyl t-butyl ether, dimethoxymethane and diethyl ether, chlorohydrocarbons, e.g. methylene chloride, esters, e.g. ethyl acetate, alcohols, e.g. tert-butanol, hydrocarbons, e.g. toluene, cyclohexane, heptane, and also dimethyl sulfoxide (DMSO), acetonitrile.

20

The alcohol to be oxidized can be used in concentrations of between 0.1 to 100% by weight, based on reaction component 1, preferably between 20 to 100% by weight.

25

In a further preferred embodiment of the reaction in multiphasic systems, the process according to the invention is carried out in the presence of one or more phase transfer catalysts. Suitable phase transfer catalysts are known to those skilled in the art (see, for example, "Phase transfer catalysis", ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY, 6th Edition electronic release, 2002). Preferred phase transfer catalysts are quaternary ammonium salts, for example

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tetrabutylammonium chloride, tetrabutylammonium
bromide, tetrabutylammonium sulfate,
methyloctylammonium chloride, methyltributylammonium
chloride, benzyltrimethylammonium chloride,
5 triethylbenzylammonium chloride, and crown ethers, e.g.
18-crown-6.

The phase transfer catalyst can be used in amounts of
between 0.1 to 10 mol%, based on the alkyne alcohol to
be oxidized, when the process according to the
10 invention is carried out in the presence of an aqueous
and also of at least one organic phase. The phase
transfer catalyst may be disposed in the initial
charge, but can also be added to the reaction component
1 or 2.

15 The process according to the invention can be carried
out in batch mode or in the form of a continuous
reaction.

20 In a preferred embodiment of the process according to
the invention, the phases involved in the reaction are
added continuously.

In this case, alkyne alcohol and hypohalite are added
25 in the form of a continual addition in accordance with
the invention and the resulting reaction solution is
simultaneously removed continuously from the reactor.

The nitroxyl compound is likewise added continuously or
30 used in the form of a steady-state phase. The favorable
pH range for the reaction can be maintained by
continuous metered addition by which bases or acids are
added to the reaction mixture in such a way that there
is a constant pH of > 7 in the reaction mixture.

The continuous reactors which are suitable for continuous reaction are known to those skilled in the art. An overview of the most important embodiments can be found, for example, in "Ullmann's Encyclopedia of Industrial Chemistry", Vol. B4.

Preferred embodiments of a process carried out continuously are continuous stirred reactors, continuous loop reactors, continuous stirred tanks or stirred tank batteries or a process carried out with the aid of centrifugal pumps.

When the process according to the invention is carried out continuously, the residence time set is between 0.1 sec and 10 h, preferably between 1 sec and 1 h, more preferably between 1 sec and 20 min.

When the process described is performed as a continuous process, this allows the additional advantages of efficient heat dissipation from the strong exothermic reaction process.

The relative ratio of the volume streams of the two reaction components can be kept constant, but can also be changed depending on the contents which are established in the reaction mixture of yet to be converted alkyne alcohol, alkynoic acid and oxidant.

The metering rate of the two reaction components is preferably such that the reaction mixture remains within the preferred temperature range, taking into account the available cooling performance.

The advantages of the process according to the invention are the provision of a process for oxidizing

alkyne alcohols which is simple to carry out from a technical point of view and uses the inexpensive oxidant hypohalite, and solves the problems known from the prior art.

5

In particular, the combination of measures of controlling the pH of the aqueous phase of the reaction mixture and of continually adding the two reactants hypohalite and alkyne alcohol to the reaction mixture
10 allow high yields of alkynecarboxylic acids to be achieved.

By the process according to the invention, using inexpensive bleaching liquor (e.g. sodium hypochlorite) which is easy to use from a technical point of view, it
15 is possible to oxidize even readily water-soluble alkynols and alkynols having terminal alkyne groups in a technically simple manner and outstanding yield to the corresponding alkynecarboxylic acids.

20 Especially substrates having terminal alkyne groups were hitherto not obtainable by the reactions which could be realized on the industrial scale and were economically viable in oxidative processes known from the prior art.

25

In addition, the process according to the invention is applicable to a wide range of substrates having terminal and nonterminal alkyne groups.

30 For example, propiolic acid can be obtained by the process according to the invention from propargyl alcohol in a 75-90% yield, and acetylenedicarboxylic acid from butynediol in a 50-70% yield.

- The wastewater resulting from the reaction contains only salts such as NaCl which are easily disposed of and can therefore be disposed of without any problem. The process according to the invention also avoids the
- 5 safety risk of large initial charges of alkynols which, in the event of metering errors of the oxidant, may lead to uncontrolled reactions (for example to the formation of chloroalkyne compounds).
- 10 The oxidative processes known from the prior art were only possible in batch mode and therefore of little interest with regard to industrial scale realizability and economic viability.
- 15 All of the above symbols of the above formulae are each defined independently of one another.

The examples which follow serve to further illustrate the invention.

Comparative example 1: Oxidation of 2-propyn-1-ol to propiolic acid with the initial charging of all of the alkyne alcohol

19.6 g (350 mmol) of 2-propyn-1-ol are dissolved
5 together with 3.0 g (17.4 mmol) of 4-hydroxy-TEMPO and
5.9 g (17.5 mmol) of tetrabutylammonium hydrogensulfate
in 132 ml of water and 132 ml of CH_2Cl_2 and cooled to
5°C (reaction component 1).

14.0 g (350 mmol) of NaOH are dissolved in 427 g of
10 2.4 M (approx. 350 ml, 840 mmol) of sodium hypochlorite
solution (technical bleaching liquor; pH 14) and cooled
to 5°C (reaction component 2).

All of reaction component 1 is initially charged in a
flask with mechanical stirrer and jacket cooling.

15 Reaction component 2 is added in such a way that the
internal temperature does not rise above 10°C. During
this time, the pH of the reaction mixture is maintained
between pH 8 and pH 10 by adding 20% sulfuric acid.

On completion of addition, stirring is continued at
20 10°C for a further 10 min. An analysis of the two
phases shows that approximately 91% of the alcohol used
has been converted. The organic phase contains 1.3 mol%
of propargyl propiolate. The aqueous phase contains
46 mol% of propiolic acid.

25

Example 1: Oxidation of 2-propyn-1-ol to propiolic acid in a biphasic system and in the presence of phase transfer catalyst

19.6 g (350 mmol) of 2-propyn-1-ol are dissolved
30 together with 3.0 g (17.4 mmol) of 4-hydroxy-TEMPO in
20 g of CH_2Cl_2 (reaction component 1).

14.0 g (350 mmol) of NaOH are dissolved in 436 g of
2.4 M (approx. 357 ml, 857 mmol) of sodium hypochlorite

solution (technical bleaching liquor; pH 14) and cooled to 5°C (reaction component 2).

In a flask equipped with mechanical stirrer, 5.9 g (17.4 mmol) of tetrabutylammonium hydrogensulfate are initially charged in 132 ml of water and 132 ml of CH₂Cl₂, and cooled to 5°C. Reaction component 1 and 2 are added in parallel with good stirring and cooling in such a way that the internal temperature does not rise above 10°C. During this time, the pH of the reaction mixture is kept between pH 8 and pH 10 by adding 20% by weight sulfuric acid.

On completion of addition, stirring is continued at 10°C for a further 10 min.

After removing the organic phase (contains the phase transfer catalyst), the aqueous phase is adjusted to pH 0 using hydrochloric acid (20% by weight) and extracted three times using 100 ml of ethyl acetate each time. The aqueous phase is discarded.

The ethyl acetate phases are combined and, after partial distillative removal of the ethyl acetate, provide an approx. 50% solution of propiolic acid in ethyl acetate which contains 19.5 g (278 mmol) of propiolic acid (yield 79 mol%).

Example 2: Oxidation of 2-propyn-1-ol to propiolic acid in a biphasic system without phase transfer catalyst

19.6 g (350 mmol) of 2-propyn-1-ol are dissolved together with 3.0 g (17.4 mmol) of 4-hydroxy-TEMPO in 20 g of CH₂Cl₂ and cooled to 5°C (reaction component 1). 14.0 g (350 mmol) of NaOH are dissolved in 440 g of 2.3 M (approx. 360 ml, 828 mmol) of sodium hypochlorite solution (technical bleaching liquor; pH 14) and cooled to 5°C (reaction component 2).

A glass flask equipped with mechanical stirrer is initially charged with 132 ml of water and 132 ml of CH_2Cl_2 , and cooled to 5°C. Reaction component 1 and reaction component 2 are added in parallel with intensive stirring and cooling in such a way that the internal temperature does not rise above 10°C. In parallel, continual addition of 20% by weight sulfuric acid keeps the pH of the reaction mixture between 8 and 10.

On completion of addition, stirring is continued for another 10 min.

After removal of the organic phase (contains 4 mol% of propargyl propiolate), the aqueous phase is adjusted to pH 0 using hydrochloric acid (20% by weight) and extracted three times with 100 ml of ethyl acetate each time. The aqueous phase is discarded.

The ethyl acetate phases are combined and, after partial distillative removal of the ethyl acetate, provide an approx. 50% solution of propiolic acid in ethyl acetate which contains 18.3 g (261 mmol) of propiolic acid (yield 75 mol%).

Example 3: Oxidation of 2-propyn-1-ol to propiolic acid in an aqueous monophasic system

19.6 g (350 mmol) of 2-propyn-1-ol are dissolved together with 3.0 g (17.4 mmol) of 4-hydroxy-TEMPO in 20 ml of water (reaction component 1).

14.0 g (350 mmol) of NaOH are dissolved in 440 g of 2.4 M (approx. 360 ml, 864 mmol) of sodium hypochlorite solution (technical bleaching liquor; pH 14) and cooled to 5°C (reaction component 2).

A glass flask equipped with mechanical stirrer is initially charged with 132 ml of water and cooled to 5°C. Reaction component 1 and reaction component 2 are

added in parallel with intensive cooling and stirring in such a way that the internal temperature does not rise above 10°C. In parallel, continual addition of 20% by weight sulfuric acid keeps the pH of the reaction mixture between 8 and 10.

On completion of the addition of the reaction components, stirring is continued for a further 10 min and any hypochlorite still present is destroyed using the sodium hydrogensulfite solution.

The reaction mixture is extracted using 150 ml CH_2Cl_2 . After removing the organic phase (contains 0.9 mol% of propargyl propiolate), the aqueous phase is adjusted to pH 0 using hydrochloric acid (20% by weight) and extracted three times using 100 ml of ethyl acetate each time. The aqueous phase is discarded.

The ethyl acetate phases are combined and, after partial distillative removal of the ethyl acetate, provide an approx. 50% solution of propiolic acid in ethyl acetate which contains 20.3 g (290 mmol) of propiolic acid (yield 83 mol%). This solution can be used directly for the preparation of ethyl propiolate. To obtain pure propiolic acid, this solution is admixed with 100 ml of toluene and then ethyl acetate is distilled off. The propiolic acid is then isolated from the remaining solution by distillation.

Example 4: Continuous oxidation of 2-propyn-1-ol to propiolic acid

56.1 g (1000 mmol) of 2-propyn-1-ol are dissolved, together with 8.6 g (50 mmol) of 4-hydroxy-TEMPO in 168 g of water (reaction component 1).

1813 g of 1.8 M (approx. 1450 ml, 2610 mmol) of sodium hypochlorite solution (technical bleaching liquor;

pH 14) cooled to 5°C are prepared (reaction component 2).

The reaction apparatus consists of a 250 ml reaction vessel which is equipped with bottom outlet, jacket cooling and mechanical stirrer and, to improve the cooling performance, is connected to an external cooler, through which the reaction mixture is pumped continually.

The apparatus is initially charged with 350 ml of 0.1 M phosphate buffer (pH 7) and cooled to 5°C.

With vigorous stirring, reaction component 1 at 1.9 g/min (corresponding to 8.2 mmol of 2-propyn-1-ol/min) and reaction component 2 at 15 g/min (corresponding to 22 mmol hypochlorite/min) are pumped into the reaction vessel, from which corresponding portions of the reaction mixture are continuously removed.

The temperature is kept between 5 and 10°C by cooling. The pH of the reaction mixture is kept at 8.5 with the aid of a titrator which supplies 20% by weight sodium hydroxide solution.

An analysis of the collected product solution shows that a total of 58 g (828 mmol) of propiolic acid have been formed (yield 83 mol%).

Example 5: Oxidation of 2-butyn-1-ol to 3-methylpropiolic acid in a biphasic system and in the presence of phase transfer catalysts

12.3 g (175 mmol) of 2-butyn-1-ol are dissolved together with 1.5 g (8.7 mmol) of 4-hydroxy-TEMPO in 13 g of CH₂Cl₂ (reaction component 1).

7.0 g (175 mmol) of NaOH are dissolved in 220 g of 2.4 M (approx. 180 ml, 432 mmol) of sodium hypochlorite

solution (technical bleaching liquor; pH 14) and cooled to 5°C (reaction component 2).

In a flask equipped with mechanical stirrer, 3.5 g (8.7 mmol) of Aliquot 336 are initially charged in 66 ml of water and 66 ml of CH₂Cl₂, and cooled to 5°C. Reaction components 1 and 2 are added in parallel with good stirring and cooling in such a way that the internal temperature does not rise above 10°C. During this time, the pH of the reaction mixture is kept between pH 8 and pH 10 by adding 20% by weight sulfuric acid.

On completion of addition, stirring is continued at 10°C for a further 10 min.

After removal of the organic phase (contains 9 mol% of 3-methylpropional), the aqueous phase is adjusted to pH 0 using hydrochloric acid (20% by weight) and extracted three times using 50 ml of ethyl acetate each time. The aqueous phase is discarded.

The ethyl acetate phases are combined and, after partial distillative removal of the ethyl acetate, provide an approx. 50% solution of 3-methylpropionic acid in ethyl acetate which contains 12.1 g (144 mmol) of 3-methylpropionic acid (yield 82 mol%).

Example 6: Oxidation of 2-butyne-1-ol to 3-methylpropionic acid in a biphasic system

12.3 g (175 mmol) of 2-butyne-1-ol are dissolved together with 1.5 g (8.7 mmol) of 4-hydroxy-TEMPO in 13 g of CH₂Cl₂ (reaction component 1).

7.0 g (175 mmol) of NaOH are dissolved in 220 g of 2.4 M (approx. 180 ml, 432 mmol) of sodium hypochlorite solution (technical bleaching liquor; pH 14) and cooled to 5°C (reaction component 2).

A flask equipped with mechanical stirrer is initially charged with 66 ml of water and 66 ml of CH_2Cl_2 , and cooled to 5°C. Reaction components 1 and 2 are added in parallel with good stirring and cooling in such a way that the internal temperature does not rise above 10°C. During this time, the pH of the reaction mixture is kept between pH 8 and pH 10 by adding 20% by weight sulfuric acid.

On completion of addition, stirring is continued at 10°C for another 10 min.

After removal of the organic phase (contains 35 mol% of 3-methylpropional), the aqueous phase is adjusted to pH 0 using hydrochloric acid (20% by weight) and extracted three times with 50 ml of ethyl acetate each time. The aqueous phase is discarded.

The ethyl acetate phases are combined and, after partial distillative removal of the ethyl acetate, provide an approx. 50% solution of 3-methylpropionic acid in ethyl acetate which contains 5.8 g (69 mmol) of 3-methylpropionic acid (yield 39 mol%).

Example 7: Oxidation of 2-propyn-1-ol to propiolic acid in an aqueous monophasic system using an aqueous initial charge and batchwise addition of the reactants
30 g (535 mmol) of 2-propyn-1-ol are dissolved together with 4.6 g (26.7 mmol) of 4-hydroxy-TEMPO in 30 g of water (reaction component 1).

625 g of 2.4 M (approx. 500 ml, 1 200 mmol) of sodium hypochlorite solution (technical bleaching liquor; pH 14) cooled to 5°C are prepared (reaction component 2).

In a 2 l glass flask equipped with mechanical stirrer, 17.8 g (100 mmol) of $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ are dissolved in 800 ml of water, adjusted to pH 7 using phosphoric acid and

cooled to 5°C. With intensive cooling and stirring, in each case approx. 45 ml of reaction component 2 and approx. 6 ml of reaction component 1 are added dropwise in alternation in such a way that the internal
5 temperature does not rise above 10°C. In parallel, the continual addition of 20% by weight sodium hydroxide solution keeps the pH of the reaction mixture between 7 and 10.

On completion of addition of the reaction components,
10 stirring is continued for a further 10 min. Evaluation of the propiolic acid content of the aqueous phase by means of HPLC gives a crude yield of 90 mol% of propiolic acid.

The reaction mixture is extracted using 300 ml CH₂Cl₂.
15 After removing the organic phase, the aqueous phase is adjusted to pH 0 using hydrochloric acid (20% by weight) and extracted three times with 300 ml of ethyl acetate each time. The aqueous phase is discarded.

The ethyl acetate phases are combined and, after
20 partial distillative removal of the ethyl acetate, provide an approx. 50% solution of propiolic acid in ethyl acetate which contains 31.2 g (446 mmol) of propiolic acid (yield 83 mol%).

25 **Example 8: Oxidation of 2-butyne-1,4-diol to acetylene-dicarboxylic acid in an aqueous monophasic system using acetamido-TEMPO**

14.4 g (167 mmol) of 2-butyne-1,4-diol are dissolved together with 2.14 g (10.0 mmol) of 4-acetamido-TEMPO
30 in 94 ml of water (reaction component 1).

6.68 g (167 mmol) of NaOH are dissolved in 337 ml (0.741 mol) of sodium hypochlorite solution (approx. 2.2 M technical bleaching liquor; pH 14) and cooled to 5°C (reaction component 2).

A flask equipped with mechanical stirrer is initially charged with 50 ml of water and cooled to 3°C. Reaction components 1 and 2 are added in parallel with good stirring and cooling in such a way that the internal
5 temperature does not rise above 10°C. During this time, the pH of the reaction mixture is kept in the range from 8.5 to 10 by adding 20% sodium hydroxide solution. A total of approx. 15 ml of sodium hydroxide solution are consumed.

10 On completion of addition, stirring is continued for another 20 min.

The reaction mixture contains 11.4 g of acetylenedicarboxylic acid in solution and 2.1 g of acetylenedicarboxylic acid in the precipitate formed (overall
15 yield 13.5 g, 71%). Extraction is effected using 300 ml of MTBE, then the pH of the aqueous reaction mixture is adjusted to pH 0 with stirring in an ice bath using conc. sulfuric acid, and extraction is effected by shaking 3 times using 100 ml of MTBE each time. The
20 MTBE extracts of the acidic reaction mixture are concentrated by evaporation. 11.1 g of acetylenedicarboxylic acid are obtained in the form of a colorless solid.

What is claimed is:

1. A process for preparing alkynecarboxylic acids,
characterized by the oxidation
5 of an alkyne alcohol
with a hypohalite
10 in the presence of a nitroxyl compound
at a pH of less than 7
with continual addition of the alkyne alcohol and
15 of the hypohalite to the reaction mixture.
2. The process as claimed in claim 1, wherein the
reaction is carried out in a multiphasic system.
- 20 3. The process as claimed in claim 2, wherein at
least one phase transfer catalyst is used.
4. The process as claimed in claims 1 to 3, wherein
the reaction mixture is removed continuously.
- 25 5. The process as claimed in claims 1 to 4, wherein
the pH of the aqueous phase of the reaction
mixture is between 7 and 11.
- 30 6. The process as claimed in claims 1 to 5, wherein
the nitroxyl compound used is 4-hydroxy-TEMPO.
7. The process as claimed in claims 1 to 6, wherein
the reaction temperature is between -5°C and 20°C.

8. The process as claimed in claims 1 to 7, wherein from 2 to 3 mol equivalents of the hypohalite are used based on the number of functional groups to be oxidized.

5

9. The process as claimed in claims 1 to 8, wherein the alkyne alcohol used is 2-propyn-1-ol or 2-butyne-1,4-diol.

- 10 10. The process as claimed in claims 1 to 9, wherein the reaction is carried out in the presence of phosphate buffer or calcium carbonate.

Abstract:

The invention describes processes for preparing alkyne-carboxylic acids characterized by the oxidation of an alkyne alcohol with a hypohalite in the presence of a nitroxyl compound at a pH of greater than 7 with continual addition of the alkyne alcohol and of the hypohalite to the reaction mixture.